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Theoretical studies in rotational isomerism

D. BHAUMIK AND G. S. KASTHA

Optics Department, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700032.

The conformational characteristics of the molecules of ethane, a few halo alkanes, acetyl and halo-acetyl halides and some unsaturated aldehydes as regards the number of stable rotamers, their relative energy differences, the barrier to hindered rotation and the dipole moment have been studied by using INDO, CNDO/2 and PCILO methods. In a few cases *ab-initio* calculations with minimal STO-3G basis set have also been made in order to assess the relative suitability of these methods in investigating rotational behaviour of moderately large molecules. The results obtained have been compared with the corresponding experimental values available from the literature. Though all these methods predict the existence of the same rotamers for any of the molecules the PCILO method in general gives better results in respect of dipole moment and energy barrier values in the case of molecules containing halo-atoms. In these cases the *ab-initio* calculations seem superior for the determination of the relative energy differences between the rotamers. In the remaining compounds this method yields values of potential barrier which are in good accord with the experimental results.

1. INTRODUCTION

Methods of Raman and infrared spectroscopy, microwave absorption, electron diffraction, N. M. R. spectroscopy and ultrasonic absorption have been used for studying the characteristics of rotational isomerism in many aliphatic molecules and from the data the number of rotamers possible, their relative energy differences and the barrier to hindered rotation have been determined. Empirical model calculations (Heublein *et al* 1970; Allet *et al* 1967; Abraham and Parry 1969; Kreevoy & Mason 1957; Miyagawa 1954) have been made to compute the rotational potential barrier and the relative energy differences between the rotamers of a molecule by considering various interaction energies between the atoms of the molecule. Though the results obtained are fairly good, they are not of general validity because of the large number of parameters involved Though ab-initio quantum theoretical calculations of the properties of the rotational isomers in ethane and a number of simple aliphatic molecules have been reported by a number of workers (Allen & Basch 1971; Radom

et al 1972; Palke 1972) using Gaussian basis set of different sizes, and some limited calculations in the case of acetyl halides and halo-acetyl halides using CNDO/2 method have appeared in the literature (Mollendal 1972), none of these calculations included many of the molecules for which fairly extensive experimental data are available.

Therefore, a programme for the calculation of the different characteristics of the rotamers of molecules of moderate sizes was undertaken by using the different approximate methods available for computing the ground state properties. In the present communication the results obtained in the case of ethane and some halo-substituted alkanes, unsaturated aldehydes, acetyl halides and also of halo-acetyl halides, where the molecules contain only one effective axis of rotation, have been reported.

2. Methods of Calculations and Results

Perturbative configuration interaction using localized orbitals (PCILO) method (Diner *et al* 1969) has been used in the calculations for molecules containing atoms upto fluorine and the method has been modified in the case of molecules containing one or more atoms of chlorine. The difficulties for the extension of this method in this case have been overcome by ignoring the 3*d*-valence shells of chlorine because the energies of the 3*d*-shells are well above the energy of the 4s-shell. *Ab-initio* calculations with minimal STO-3G basis set (Hehre *et al* 1969) have been performed for several molecules in which the positions of energy extrema were obtained by the PCILO method. Ground state properties for a few molecules were also computed using CNDO/2 and INDO methods (Pople & Segal 1965; Pople & Beveridge 1970) in order to ascertain their usefulness in case of moderately large molecules. In all of these methods, except in the *ab-initio* calculations, the total ground state energy and dipole moment of a molecule were calculated for each of the configurations resulting from the variation of the dihedral angle by intervals of 60°. In some cases a smaller step of 30° was also used. It was found that the methyl group in 1, 2-dichloropropane, 2-chlorobutane and crotonaldehyde molecules takes a staggered arrangement which corresponds to minimum energy of the configurations of these molecules with respect to the orientation of the group.

Internal geometrical parameters required for the molecules have been taken from the published literature (Shimanouchi & Suzuki 1961; Pennington *et al* 1956; Khan & Jonathan 1970; Sinnott 1961). The computed values for rotational energy barriers, energy differences between the different rotamers, the dipole moments for the stable conformers have been mentioned in appropriate places and compared with the experimental values of these quantities wherever available.

3. Discussions

Results obtained for the various molecules by different methods of calculations are briefly discussed in the following paragraphs.

Ethane

The staggered rotamer is found to be the most stable form in ethane, according to all the four methods. The value of the rotational barrier determined by the PCILO, CNDO/2 and INDO methods lies between 2.0-2.2 kcal/mol. which is somewhat smaller than the value 3.2 kcal/mol obtained from the ab-initio calculation. The last value fairly agrees with the experimental value 2.93 kcal/mol (Weiss and Leroi 1968) and the value 3.3 kcal/mol calculated by ab-initio method using extended basis set (Palke 1972).

1, 2-difluoroethane

The variation of the ground state energy of the molecule with the dihedral angle is depicted in figure 1, which shows two energy minima corresponding

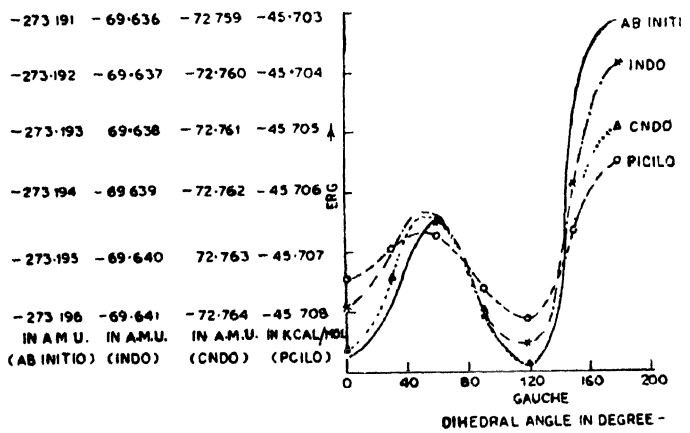

Figure 1. Variation of the ground state energy of 1, 2-difluoroethane with the dihedral angle

to the usual trans and gauche forms. According to all the methods the gauche form is found to be stabler than the trans form by a few hundred cal/mol. Klaboe & Nielsen (1960) reported that the two rotamers are of almost equal energy while Abraham & Kemp (1971) obtained a value of 600 cal/mol for the energy difference between the trans and the stabler gauche forms. This is close to the value of 744 cal/mol derived from the PCILO method. The value of the dipole moment calculated by the different methods lies between 1.85-2.99D which is somewhat smaller than the experimentally reported value 3.10D (Abraham & Kemp 1971).

1, 2-dichloroethane

Both PCILO and ab-initio calculations suggest the existance of two stable rotamers trans and gauche in this molecule (fig. 2). The former method does not show any energy difference between them while according to the latter method the *trans* form is more stable than *gauche* form by about 2.07 kcal/mol which may be compared with the experimental value 1.15 ± 0.15 kcal/mol (Sheppard 1959). Dipole moment of the *gauche* rotamer calculated by the two methods are 3.2 and 3.6D respectively and are somewhat higher than the experimental value 2.55D (Mizushima 1954).

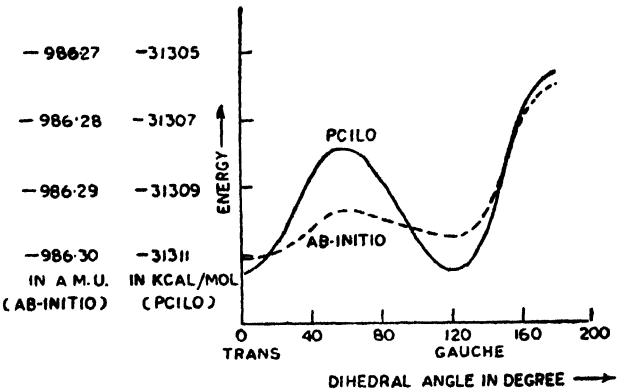

Figure 2. Variation of the ground state energy of 1,2-dichloroethane with the dihedral angle

The trans-gauche and gauche-gauche potential barrier calculated by PCILO method are respectively 3.74 and 5.9 kcal/mol and the corresponding values obtained from ab-initio calculations are 4.64 and 14.04 kcal/mol respectively. It may be noted that Mizushima (1954) inferred the lower barrier to be about 3 kcal/mol and the other barrier to be much higher. Ultrasonic absorption measurement in liquid yielded a value of 3.2 kcal/mol (Piercy 1965). Other experimental values reported are 2.0 and 6.7 kcal/mol for these two barriers respectivety (Ref. 22, Heublein 1970).

1, 1, 2-trichloroethane

The ground state energy of the molecule calculated by the PCILO method shows three minima, two of which are due to the two indistinguishable trans conformers while the third one corresponds to the gauche isomer. This method does not give any information about the energy difference between these two rotamers but, the computed values for trans-trans and trans-gauche potential barriers are respectively 4.49 and 6.64 kcal/mol. The corresponding experimental values, obtained from the ultrasonic absorption measurements (Lamb 1960)., are 5.8 and 7.9 kcal/mole respectively.

1, 2-dichloropropane

The existence of three rotamers T, G1 and G2 (Dempster *et al* 1969) is apparent from the results of calculations using the PCILO method. The values of relative energy difference between these rotamers obtained from ab-initio calculations show, that of the three rotamers, the T-conformer is the most stable and the energies of the other two forms are higher by 1.06 and 2.07 kcal/mol respectively. These values are in good agreement with the corresponding experimental values 1.2 and 1.9 kcal/mol reported by Dempster *et al* (1969). The T-G1, G2-G1 and T-G2 barriers calculated by the PCILO method are respectively 3.95, 6.09 and 5.00 kcal/mol. The analysis of ultrosonic absorption data due to the liquid in terms of two positions of equlibrium yielded a value of 5.8 kcal/mol (Lamb 1960) which is of the same magnitude as obtained in this calculation.

2—Chlorobutane

Both PCILO and ab-initio calculations show that the molecule has three ratational isomers (fig. 3) of which the conformer where the two methyl groups are trans to each other has the lowest energy. This is in accordance with the experimental results of Benedetti and Cecchi (1972) and of Ukaji and Bonham (1962). The energies of the other two forms, in which the methyl group is trans

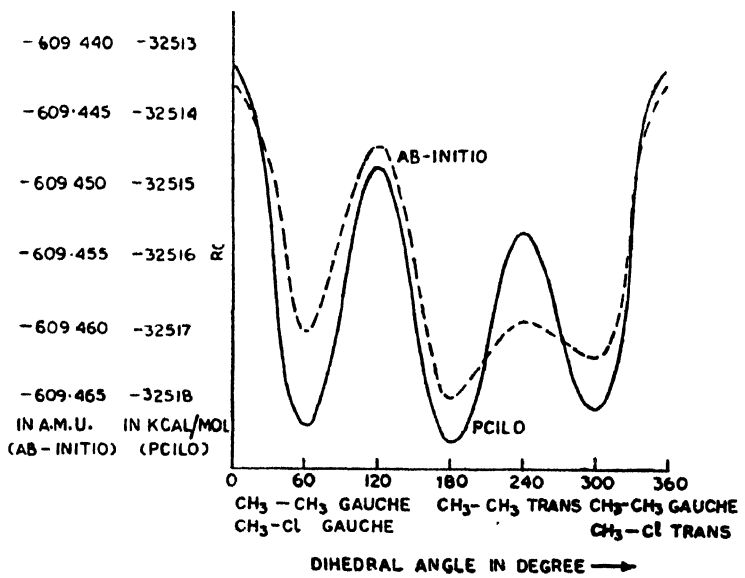

Figure 3. Variations of the ground state energy of 2-chlorobutane with the dihedral angle.

to the chlorine atom and gauche to both the chlorine atom and methyl group, according to PCILO calculations are respectively higher than the most stable

conformer by 474 and 231 cal/mol. These are of the same order (415 cal/mol) as estimated from electron diffraction measurements (Ukaji and Bonham 1962), but this agreement is apparent for according to the same authors the estimate is subject to large errors. The ab-initio method on the other hand gives the values 1.9 and 2.9 kcal/mol for the same quantities and though these values appear large, they are approximately of the same order as found in the case of 1, 2-dichloropropane. The rotational barrier between the higher energy conformers obtained from the PCILO method is 5.1 kcal/mol and the corresponding value given by the ab-initio calculations is 12.0 kcal/mol. The reported experimental value 5.4 kcal/mol (Mason 1965) is nearer to the PCILO result but this correspondance is not certain because the author has not identified the conformers separated by this barrier.

Unsaturated aldehydes

In each of the two aldehydes, acrolein and crotonaldehyde, the calculations show the existence of the two rotamers *s*-trans and *s*-cis. The s-trans is found to be the most stable conformer according to both the PCILO and ab-initio methods.

Table 1. Experimental and calculated values of the energy difference, rotational barrier and the dipole moment of acrolein and crotonaldehyde

Molecules	Energy difference kcal/mol			Dipole moment, Debyes			Barrier kcal/mol		
	PCILO	*Ab-initio*	Expt.[a]	PCILO	*Ab-initio*	Expt.[a]	PCILO	*Ab-initio*	Expt.[a]
Acrolein	0.80	0.25	2.1	2.2	2.1	2.9	2.9	6.3	7.1
Crotonal-dehyde	0.80	0.56	1.9	2.5	2.53	3.5	2.85	6.3	7.4

(a) Mason (1965).

A comparison of the computed results and the corresponding available experimental data for these two molecules is presented in table 1. It is seen that the theoretical values of the energy difference betwee the rotamers of acrolein and crotonaldehyde are considerably lower than those reported by Mason (1965) in the liquid phase of these molecules, but the values of dipole moment calculated by both the methods and the barrier-height obtained from *ab-initio* calculations are fairly in agreement with the experimental results.

Acetyl halides

Computations of ground state energies for different dihedral angles have been carried out for acetyl fluoride and acetyl chloride molecules, using the PCILO method to determine their stable conformers. For acetyl fluoride molecule calculations using INDO and CNDO/2 methods have also been performed.

Table 2. Experimental and calculated values of the barrier-height and dipole moment of acetyl fluoride and acetyl chloride

Molecule	Barrier in cal/mol					Dipole moment in Debyes				
	Ours					Ours				
	PCILO	INDO	CNDO/2	Others[a]	Expt.	PCILO	INDO	CNDO/2	Others[a]	Expt.
Acetyl fluoride	560	502	502	627	1041[b]	2.3	2.79	2.79	2.53	2.96[b]
Acetyl Chloride	1088			207	1296[c]	2.35			2.79	2.38[d]

(a) Mollendal (1972).
(b) Pierce & Krisher (1959).
(c) Sinnott (1961).
(d) Zahn (1932).

The most stable rotamer of these molecules is the form in which the C—F or the C-Cl bond is in he trans position with respect to one of the three C-H bonds of the methyl—group. The relevant data concerning these two molecules are shown in table 2. The calculated results for acetyl chloride are closer to the experimental values than in the case of acetyl fluoride. It is also seen from the same table that in the case of acetyl chloride the PCILO method gives results better than that reported by Mollendal (1972) using CNDO/2 method.

Halo—acetyl halides

The results of calculations for chloroacetyl fluoride and chloroacetyl chloride molecules by the PCILO method together with the corresponding experimental data are given in table 3. The gauche rotamer is found to be more stable than the trans-rotamer in both the molecules. Mollendal (1972) also predicted from the CNDO/2 calculations that the gauche-rotamer in chloroacetyl fluoride and the cis-conformer in the chloroacetyl chloride molecule would be the more stable forms. But, according to the experimental evidences the trans-rotamer is the more stable configuration in each of the molecules and

their less stable conformer is either the cis-form or a form close to it. (Mizushima 1954; Khan and Jonathan 1969 and Nakagawa *et al* 1952). It is seen from table 3 that the presently computed values of the energy differences between the rotamers of the above two molecules show better agreement with the experimental data as compared to that reported by Mollendal (1972).

Table 3. Experimental and calculated values of the energy difference of the two stable rotamers of chloroacetyl fluoride and chloroacetyl chloride

Molecule	Ours cal/mol.	Others[a] cal/mol.	Expt.[b] cal/mol.
Chloroacetyl fluoride	738	820	760 ± 200
Chloroacetyl chloride	200	10,000	970 ± 200

(a) Mollendal (1972).

(b) Khan & Jonathan (1969).

According to the CNDO/2 method, used by him, the cisconformer is approximately 10 kcal/mol more stable than the trans form of chloroacetyl chloride.

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